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SPACE GROUPS OF CRYSTALS OF α-,β-AND γ-PICOLINE AT −180°C

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Plate III

ABSTRACT. The dimensions of the unit cell, number of molecules per unit cell and the space groups of crystals of α-, β- and γ-picoline at −180°C have been determined by studying the Debye-Scherrer patterns of the crystals. All the crystals are found to have the monoclinic lattice. The space group assigned to the α-picoline crystal is $P2/m$ with $a = 9.97$, $b = 10.91$, $c = 10.90$Å, $\beta = 111°54'$, that of β-picoline is $P2_1/m$ with $a = 6.95$, $b = 11.87$, $c = 7.05$ Å, $\beta = 94°12'$ and that of the γ-picoline crystal is $P2_1/c$ with $a = 7.21$, $b = 7.69$, $c = 10.20$ Å, $\beta = 110°42'$.

INTRODUCTION

In continuation of the previous work on the analysis of the Debye-Scherrer patterns of crystals of toluene (Biswas and Sirkar, 1957), pyridine (Biswas, 1958), chlorobenzene and bromobenzene (Biswas, 1958), 1, 3, 5-trichlorobenzene (Biswas, 1957) and ortho-, meta- and paraxylene (Biswas, 1960), the present investigation was undertaken to study the Debye-Scherrer patterns of α-, β- and γ-picoline at −180°C and to find out the dimensions of the unit cell, number and molecules per unit cell and the space group to which the crystals belong.

EXPERIMENTAL

The Debye-Scherrer patterns of crystals of α-, β- and γ-picoline at −180°C were photographed with a low temperature camera used previously (Biswas, 1958). The radius of the camera was derived from the Debye-Scherrer pattern of Al powder and it was found to be 4.50 cm. A Seifert X-ray tube running at 32 KV and 26 mA was used to photograph the patterns. An exposure of three and half hours using Cu Kα radiation was sufficient to record the patterns with appropriate density.

RESULTS AND DISCUSSION

In determining the dimensions of the unit cells of the crystals of these isomers Ito's method (Ito, 1950) was applied and all the crystals were found to belong to the monoclinic system. The crystals could not be assigned to any lattice of

symmetry higher than that of the monoclinic system. Lipson's method (Lipson, 1949) was also tried, but significant constant differences in the values of $\sin^2\theta$ were not observed.

α-Picoline : The Debye-Scherrer pattern due to crystals of α-picoline at −180°C is reproduced in **Fig. 1**, Plate III. The values of $Q\ (1/d^2_{hkl})$, where d_{hkl} is the spacing of the direct lattice calculated from the Debye-Scherrer rings are tabulated in column 1, Table I. The dimensions of the unit cell of the reciprocal lattice which are found to explain all the observed Q-values satisfactorily are :

$a^* = 0.0916$ $\quad\quad$ $\alpha^* = 59°42'$

$b^* = 0.0988$ $\quad\quad$ $\beta^* = 90°$

$c^* = 0.1161$ $\quad\quad$ $\gamma^* = 90°$

The values of Q observed from the photograph and those calculated with the dimensions of the unit cell given above, the intensities and the proposed indices for the reciprocal lattice are also given in Table I. The dimensions of the unit cell of the direct lattice corresponding to the reciprocal lattice are :

$a = 9.97$ Å

$b = 10.92$ Å $\quad\quad$ $\beta = 120°18'$

$c = 11.70$ Å

The above cell was reduced further (Buerger, 1958) and the dimensions of the reduced cell are :

$a = 9.97$ Å

$b = 10.92$ Å $\quad\quad$ $\beta = 111°54'$

$c = 10.90$ Å

The indices referred to this reduced direct lattice are given in the last column of Table I.

On examining the powder pattern, it was noticed that there was some indication of the preferential orientation of the crystallites with a particular axis orientated around the vertical axis of the specimen. The primitive translation along the preferred axis is found to be about 10.94 Å. This value agrees with the length either of the *b*-edge or of the *c*-edge of the reduced unit cell. The positions of the diffraction maxima on the different layer lines, however, indicate that the prefered axis is the *b*-axis. The layer lines in which the different maxima due to reflections from planes of different indices are actually present are given in Table II. The positions of the maxima in the different layer lines thus confirm the correctness of the indices assigned to the corresponding reflecting planes.

To determine the number of molecules per unit cell the density of the substance at −180°C was determined by the method described earlier (Biswas and

TABLE I

Indexing of the powder pattern of α-picoline crystals

Q (observed)	*Q* (calculated)	*h'k'l'* (reciprocal lattice)	*hkl* (reduced direct lattice)
0.0293 (m)	0.0293	021	101
0.0335 (m)	0.0336	200	020
0.0345 (m)	0.0348	011	20̄1
0.0378 (w)	0.0377	121	111
0.0388 (w)	0.0390	020	200
0.0420 (m)	0.0416	20̄2	102
0.0435 (s)	0.0434	210	120
	0.0433	111	211
0.0475 (m)	0.0476	120	002
	0.0471	201	210
			121
0.0542 (s)	0.0540	002	202
0.0665 (m)	0.0665	03̄1	201
0.0680 (s)	0.0685	211	221
0.0755 (s)	0.0759	021	030
	0.0756	300	301
0.0808 (w)	0.0802	222	022
	0.0806	13̄2	112
0.0880 (m)	0.0876	202	031
		030	300
			222
0.0956 (m)	0.0962	130	310
	0.0954	112	
0.1046 (w)	0.1048	113	131
0.1162 (w)	0.1162	312	132
0.1172 (w)	0.1172	042	202
			222
0.1251 (w)	0.1247	122	123
0.1350 (vw)	0.1344	400	040
			401
0.1390 (vw)	0.1391	043	103
	0.1394	022	402
0.1628 (w)	0.1633	330	330
	0.1622	024̄	410
0.1732 (m)	0.1634	420	240
	0.1730	222	123
0.1890 (w)	0.1886	240	420
	0.1884	402	004
0.2086 (w)	0.2090	312	702
			50̄2
0.2302 (w)	0.2301	023	430
0.2551 (m)	0.2559	403	205
0.3025 (w)	0.3024	600	060
0.3230 (w)	0.3226	151	151

TABLE II

Layer line	Indices for the maxima present
Zero layer line	101 20$\bar{1}$ 200 10$\bar{2}$ 002 202 201
First layer line	111 21$\bar{1}$ 210 012
Second layer line	020 120 12$\bar{1}$ 22$\bar{1}$

Sirkar, 1957) and was found to be 1.134 gm cm $^{-3}$. With this value of the density and the dimensions the unit cell given above the number of molecules per unit cell was found to be 8.08. Thus the unit cell contains eight molecules.

It can be easily seen from Table I that there is no restriction regarding reflection from different planes. There is, however, no space group with eight equivalent points not showing any restriction of reflection. The space group $C^1_{2h}-P2/m$ does not show any restriction but it has only four equivalent positions with an asymmetric molecule at each position. It is evident, therefore, that there are two molecules forming an asymmetric unit at each equivalent position in the crystals of α-picoline and the space group is C^1_{2h}.

β-Picoline : The Debye-Scherrer pattern due to crystals of β-picoline at $-180°$C is reproduced in Fig. 2, Plate III. The values of Q observed from the photograph are given in column 1, Table III.

In this case the dimensions of the unit cell of the reciprocal lattice which could explain all the Q-values satisfactorily are :

$a^* = 0.1533$ $\quad \alpha^* = 90°$

$b^* = 0.2014$ $\quad \beta^* = 90°$

$c^* = 0.0843$ $\quad \gamma^* = 85°48'$

The dimensions of the unit cell of the direct lattice with b-axis as the unique axis corresponding to those of the reciprocal lattice are :

$a = 6.95$ Å

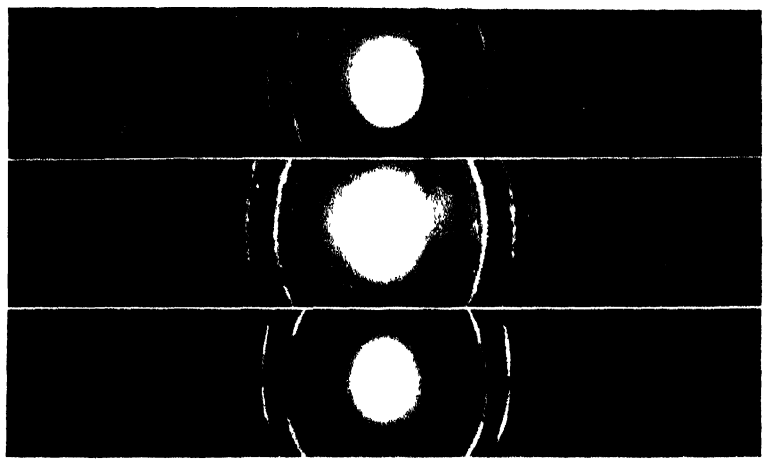
$b = 7.05$ Å

$c = 11.87$ Å

Fig. 1.

Fig. 2.

Fig. 3



Debye-Scherrer patterns

Fig. 1. α-picoline at − 180 C
Fig. 2. β-picoline at − 180 C
Fig. 3. γ-picoline at − 180 C

It can be easily seen that the above cell cannot be reduced further. So the dimensions of the unit cell of the β-picoline crystal are as given above. The indices of the planes referred to the direct lattice are given in the last column of Table III.

TABLE III

Indexing of powder pattern of β-picoline crystals

Q (observed)	*Q* (calculated)	*h'k'l'* (reciprocal lattice)	*hkl* (final direct lattice)
0.0380 (w)	0.0380	110	101
0.0440 (w)	0.0440	110	101
0.0450 (w)	0.0449	111	111
0.0495 (s)	0.0493	012	120
0.0510 (vs)	0.0509	111	111
0.0660 (vw)	0.0665	112	$12\bar{1}$
0.0724 (m)	0.0725	112	121
0.0810 (vs)	0.0808	200	002
0.0830 (vs)	0.0832	020	200
0.1020 (s)	0.1018	113	$13\bar{1}$
0.1140 (s)	0.1140	004	040
0.1338 (m)	0.1342	104	041
0.1595 (w)	0.1592	213	132
0.1705 (w)	0.1710	213	132
0.1815 (vw)	0.1818	300	003
0.1875 (vw)	0.1872	030	300
0.2060 (w)	0.2055	131	$31\bar{1}$
0.2185 (m)	0.2187	131	311
0.2515 (w)	0.2512	033	330
0.2565 (vw)	0.2560	006	060
0.2900 (m)	0.2900	224	242
0.3015 (w)	0.3012	034	340

The density of the substance at −180°C was found to be 1.098 gm cm^{-3}. The number of molecules per unit cell calculated with this density is found to be 4.01. Thus the unit cell contains 4 molecules. It can be easily seen from Table III that the conditions limiting possible reflections are :

hkl : no condition
hol : no condition
oko : $k = 2n$

So, the probable space group which can be assigned to the crystal is C^2_{2h}–$P2_1/_m$.

γ-Picoline : The Debye-Scherrer pattern due to crystals of γ-picoline at −180°C is reproduced in Fig. 3, Plate III. The Q-values observed from the photograph are given in column 1, Table IV.

The dimensions of the unit cell of the reciprocal lattice which could account for all the *Q*-values observed in this case are :

$a^* = 0.1049$ $\quad \alpha^* = 90°$
$b^* = 0.1300$ $\quad \beta^* = 69°18'$
$c^* = 0.1483$ $\quad \gamma^* = 90°$

The dimensions of the unit cell of the direct lattice corresponding to those of the reciprocal lattice after a and c axes being interchanged are :

$a = 7.21$ Å
$b = 7.69$ Å $\qquad \beta = 110°42'$
$c = 10.20$ Å

It can be easily seen that the above cell cannot be reduced further. So, the dimensions of the unit cell of the γ-picoline crystal are as given above. The indices referred to this direct lattice are given in the last column of Table IV.

TABLE IV

Indexing of the powder pattern of γ-picoline crystals

Q (observed)	Q (calculated)	$h'k'l'$ (reciprocal lattice)	hkl (final direct lattice)
0.0450 (vs)	0.0448	200	002
		201	102
0.0678 (vs)	0.0676	020	020
0.0880 (s)	0.0880	002	200
0.0888 (m)	0.0888	202	202
		201	102
0.1124 (m)	0.1124	220	022
		221	122
0.1376 (vw)	0.1381	112	211
0.1560 (s)	0.1566	022	220
	0.1564	221	122
		$32\bar{1}$	123
		$22\bar{2}$	222
0.1768 (w)	0.1768	202	202
		203	302
0.1792 (vs)	0.1792	400	004
		402	204
0.2230 (m)	0.2234	321	123
0.2456 (w)	0.2452	222	222
		401	104
		$40\bar{3}$	304
0.2466 (s)	0.2468	420	024
0.2702 (m)	0.2704	040	040
0.2922 (w)	0.2924	041	140
		$14\bar{1}$	141
0.3142 (s)	0.3146	141	141
0.3588 (vw)	0.3590	$60\bar{2}$	206
	0.3584	042	420
0.3802 (vw)	0.3805	523	325
0.4500 (m)	0.4496	440	044
0.4705 (vw)	0.4708	620	026
0.4915 (w)	0.4912	604	406
0.5432 (w)	0.5437	152	251
0.6080 (w)	0.6084	060	060
0.6228 (vw)	0.6222	044	440
	0.6234	602	206
0.7120 (m)	0.7120	523	325
0.7245 (m)	0.7241	414	414

The density of the substance at −180°C was found to be 1.163 gm cm^{-3}. The number of molecules per unit cell calculated with this density is found to be 4.03. Thus the unit cell contains four molecules.

Table IV shows that the reflections from the planes (010), (030) and (050) are absent because the Q values for these planes are 0.0169, 0.1521 and 0.4225 respectively and these do not agree with any of the observed values. Hence it is concluded that (*oko*) reflection are absent when k is odd.

The calculated values of Q_{hol} with l odd together with those observed in the neighbourhood of some of these values are given in Table V.

TABLE V

Q_{hol}	Computed	Nearest value observed	Difference
$Q10\bar{1}$	0.0222		
$Q101$	0.0442	0.0450 (002)	0.0008
$Q20\bar{1}$	0.0772		
$Q103$	0.0898	0.0888 (202)	−0.0010
$Q201$	0.1212		
$Q203$	0.1228		
$Q103$	0.1558	0.1560	0.0002
$Q301$	0.1762	0.1768	0.0006
$Q30\bar{1}$	0.2422		
$Q203$	0.2548		

The difference between Q_{002} and Q_{101} and that between Q_{103} and Q_{203} are beyond experimental error which is less than 0.0005. Hence (101) and (103) reflections are most probably absent. Reflections from the (103) planes may, however, be superposed on that from (220) and the (301) reflection may lie very close to (202) reflection, but since the other (*hol*) reflections with l odd are definitely absent it is concluded that all such reflections are absent.

Table IV then shows the following conditions limiting possible reflections :

hkl : no condition

hol : $l = 2n$

oko : $k = 2n$

So, the probable space group of the crystal is C^5_{2h} - $P2_1/c$.

Finally, it has to be pointed out that in all the cases mentioned above assignment of alternative unit cell dimensions leads to serious difficulties, because either some of the intense reflections cannot be accounted for or the number of molecules per unit cell differs considerably from whole numbers. On the other hand, with cell dimensions given above these difficulties disappear completely.

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